

AD-A040 582

GRUMMAN AEROSPACE CORP BETHPAGE N Y RESEARCH DEPT
GERMANIUM FILM PROGRAM.(U)
JUL 76 H KIVLIGHN

F/G 20/2

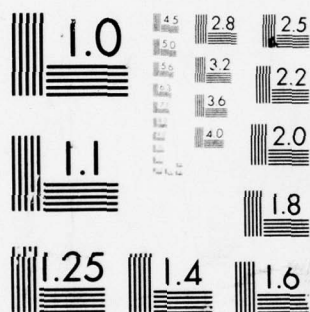
UNCLASSIFIED

RM-624

NL

1 OF 1
AD
A040582





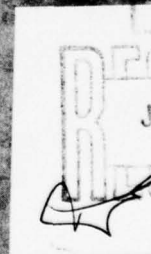
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

RM-624

GERMANIUM FILM PROGRAM

July 1976

RESEARCH DEPARTMENT



DISTRIBUTION STATEMENT

Approved for public release

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (14) RM-624	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) (6) Germanium Film Program.		5. TYPE OF REPORT & PERIOD COVERED (9) Memorandum rept.
7. AUTHOR(s) (10) Herbert Kivlighn, Jr.		6. PERFORMING ORG. REPORT NUMBER RM-624
9. PERFORMING ORGANIZATION NAME AND ADDRESS Grumman Aerospace Corporation Bethpage, New York 11714		8. CONTRACT OR GRANT NUMBER(s) N/A
11. CONTROLLING OFFICE NAME AND ADDRESS Bethpage, New York 11714		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (12) 38 p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) N/A		12. REPORT DATE Jul 1976
		13. NUMBER OF PAGES 35
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) N/A		
18. SUPPLEMENTARY NOTES N/A		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report discusses the efforts that were expended toward assessing the formation of elemental germanium films from oxygen-deficient germanate glasses. An attempt has been made to physically characterize them from the viewpoint of amorphous/crystalline content, at least in the qualitative sense. A possible mechanism of film formation is also presented. The latter		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

406 165

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

section deals with preliminary photoexcitation experiments which yielded positive reproducible photovoltage responses in some of the films.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

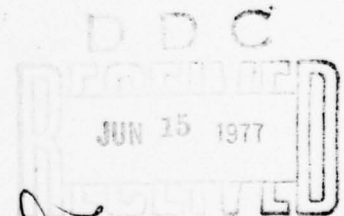
GERMANIUM FILM PROGRAM

by

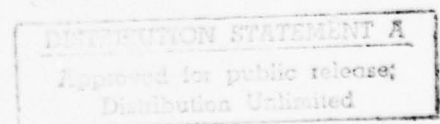
Herbert Kivlighn, Jr.

Materials and Structural Mechanics

July 1976



Approved by: *Charles E. Mack, Jr.*
Charles E. Mack, Jr.
Director of Research



ABSTRACT

This report discusses the efforts that were expended toward assessing the formation of elemental germanium films from oxygen-deficient germanate glasses. An attempt has been made to physically characterize them from the viewpoint of amorphous/crystalline content, at least in the qualitative sense. A possible mechanism of film formation is also presented. The latter section deals with preliminary photoexcitation experiments which yielded positive reproducible photovoltage responses in some of the films.

WHITE SECTION		<input checked="" type="checkbox"/>
RED SECTION		<input type="checkbox"/>
BY		
DISTRIBUTION AVAILABILITY CODES		
Dist.	1. 2. 3. 4. 5. 6. 7. 8. 9. 10.	
A		

TABLE OF CONTENTS

<u>Item</u>	<u>Page</u>
Introduction	1
Experimental Procedures	3
Glass Preparation	3
Film Preparation	4
Film Optical Characterization	4
Electrical Characterization	11
X-Ray Diffraction	11
Photoexcitation Experiments	11
Results	12
Glass Preparation	12
Film Preparation	12
Film Optical Characterization	12
Electrical Characterization	19
X-Ray Diffraction	19
Photoexcitation Experiments	19
Discussion	26
Summary	29
References	30

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Photomicrograph of Germanium Film Formed on Glass 410-I (Melt 52-K), 430°C - 6 hr 15 min/H ₂ , 1 cm = 33 μm	13
2	Photomicrograph of Germanium Film Formed on Glass 410-I (Melt 52-L), 450°C - 6 hr/H ₂ , 1 cm = 33 μm	14
3	Photomicrograph of Germanium Film Formed on Glass 410-I (Melt 52-I), 480°C - 6 hr/H ₂ , 1 cm = 33 μm	15
4	Photomicrograph of Germanium Film Formed on Glass 410-DJ (Melt 4-15), 420°C - 7 hr/H ₂ , 1 cm = 33 μm	16
5	Photomicrograph of Germanium Film Formed on Glass 410-DJ (Melt 2-3), 500°C - 7 hr/H ₂ , 1 cm = 33 μm	17
6	Photomicrograph of Germanium Film Formed on Glass 410-DJ (Melt 4-3), 600°C - 3½ hr/H ₂ , 1 cm = 33 μm	18
7	X-Ray Diffraction Pattern for Germanium Film Formed on Glass 410-I, 400°C - 24 hr/H ₂	20
8	X-Ray Diffraction Pattern for Germanium Film Formed on Glass 410-I, 500°C - 2 hr/H ₂	21
9	X-Ray Diffraction Pattern for Germanium Film Formed on Glass 410-I, 500°C - 7 hr/H ₂	22
10	X-Ray Diffraction Pattern for Glass 410-I, Untreated	23

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Theoretical Germanate Base Glass Compositions (moles)	5
2	H ₂ Treatment, 410-I (Melt 52)	6
3	H ₂ Treatment, 410-DJ	7
4	H ₂ Treatment, 410-DJ (Melt 6)	8
5	H ₂ Treatment, 410-EA (Melt 2) and 410-EC (Melt 2)	9
6	H ₂ Treatment, 410-EE (Melt 1) and 410-EF (Melt 1)	10
7	Comparison of 15 Second Exposure Δ EMF GE Film Responses (mv), Glasses 410-I, -DJ	24
8	Comparison of 15 Second Exposure Δ EMF GE Film Responses (mv), Glasses 410-DJ, -EE, -EC, -EF	25

INTRODUCTION

It is common knowledge that the methods employed in thin film formation, in general, are almost entirely based upon vapor deposition or sputtering processes. During 1974, Grumman was issued a patent (Ref. 1) which depicted a new method for forming thin films of elemental germanium. The preliminary exploratory work related to the Grumman patent has been detailed in a previous report (Ref. 2). In that effort, it had been observed that the precipitated germanium films could exhibit crystalline or amorphous character; the behavior paralleled that of vapor deposited germanium films. For example, J. F. Pócza et al. (Ref. 3) have reported that vapor deposited amorphous germanium films reveal the commencement of ordering at 350°C. Á. Barna et al. (Ref. 4) have exhibited some vivid transmission electron micrographs of the early site crystallization of amorphous germanium films. Another paper by Á. Barna et al. (Ref. 5) associates the degree of crystallization of amorphous germanium films with their electrical properties. In this work, three types of film crystallization were reported: surface crystallization, volume crystallization, and contaminated volume crystallization. Amorphous areas were present in all three types, and the conductivity varied with each crystallization type. Another investigation into the amorphous crystalline transition in germanium films was reported by J. Johannessen (Ref. 6); again the films of this study were vapor deposited. The conductivity was higher by three to four orders of magnitude when the films changed from the amorphous to the polycrystalline state. Some additional physical characteristics were reported by Á. Barna et al. (Refs. 7 and 8) for the structural behavior of vapor deposited amorphous germanium. The latter (Ref. 8)

exhibits a sharp electron micrograph for "hillock" formation in amorphous germanium. J. S. Johannessen (Ref. 9) reported on the dependence of the electrical conductivity on the thickness of thin germanium films. J. E. Fisher (Ref. 10) explored the photoelectric properties of amorphous germanium films, and M. Valkiainen et al. (Ref. 11) have noted their dielectric behavior. Another general survey of the electrical and optical properties of amorphous germanium has been reported by M. Hirose et al. (Ref. 12). H. Kallman et al. (Ref. 13) reported that thin films of germanium exhibited large photovoltages, while W. Ma et al. (Ref. 14) reported an anomalously high photovoltaic effect in these films. As has been noted previously, all of these investigations were done on vapor deposited films. However, since the films did exhibit photovoltage responses, it was felt that the precipitated germanium films prepared in our laboratory should be examined for similar characteristics.

EXPERIMENTAL PROCEDURES

GLASS PREPARATION

The base glasses utilized during this study were developed from our knowledge of oxygen deficient germanate preparations. The following chemicals were employed: electronic grade germanium dioxide, reagent grade silicon carbide, electronic grade elemental germanium powder, reagent grade arsenic pentoxide, and reagent grade antimony trioxide. Weighed amounts of the respective batch chemicals were placed together in polyethylene jars and ball-milled overnight. The melting operation was carried out in two Harop glo-bar electric fired furnaces; one unit was held in the 1200-1300°C temperature range, while the second was kept in the 1400-1500°C range. B&W Cerrox 1000 high alumina crucibles were used as the melting vessels. Small increments of the batch material were fused in the 1200-1300°C unit until all of the batch had reacted; this was necessary because the reactants produced large amounts of gas which caused crucible overflow if the 1400-1500°C furnace was the sole melting unit employed. Following the initial fusion, the crucible and reactant product were placed at the higher temperature and soaked for one to four hours. Following the soak period, the molten glass was pressed into 25-64 cm² slabs and annealed at 400°C - 1 hour and cooled in the annealing furnace overnight. Obviously, the sample size differential was related to the amount of glass remaining in the crucible after the melting process. The glass was then sectioned into 3 cm² segments. The two large surfaces of the samples were ground and polished to a glossy finish; the final polishing step utilized one micron Al₂O₃. The grinding/polishing step was necessary to rid the sample of its pressed surface and expose the

sample body which had a more uniform thermal history. Table 1 represents the theoretical batch compositions, expressed in moles, for the base glasses studied during this investigation.

Since the final base glasses resulted from unstirred melts, inhomogeneity was a constant problem. In order to assure that a glass was not completely off the composition field of interest, conventional density and refractive index measurements were utilized. Dilatometric measurements were conducted to monitor the area of the transformation range for the base glasses.

FILM PREPARATION

The germanium films were prepared in a model FH-303-A Hoskin's tube furnace that had been adapted for hydrogen treatments. The sample was suspended in the tube chamber through a porous ceramic plug. A chromel-alumel thermocouple was placed inside the tube next to the sample. The tube was flushed with argon as the furnace heated up to approximately 200°C; then the argon flow was turned off and hydrogen was introduced into the chamber. The excess hydrogen was burned off at the top of the tube. Hydrogen treatment temperatures generally varied between 400-600°C and the treatment time ranged from 10 minutes to 7 hours. The samples were weighed before and after hydrogen treatment. Table 2 represents the hydrogen treatments for glass 410-I; Tables 3 and 4 for glass 410-DJ; Table 5 for glasses 410-EA and 410-EC, with Table 6 representing the hydrogen treatments for glasses 410-EE and 410-EF.

FILM OPTICAL CHARACTERIZATION

A Reichert reflection microscope was used to examine and photograph the germanium film surface.

TABLE 1 THEORETICAL GERMANATE BASE GLASS
COMPOSITIONS (MOLES)

Code No. 410-	I	DJ	EA	EA	EC	ED	EE	EF
GeO ₂	95.0	95.0	95.0	95.0	95.0	95.0	95.0	95.0
SiC	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Ge		5.0	5.0	5.0	5.0	5.0	5.0	5.0
As ₂ O ₃ [*]			0.1	0.5	1.0			
Sb ₂ O ₃						0.1	0.5	1.0

*When calculating this actual batch weight As₂O₅ was used
as the source for As₂O₃.

TABLE 2 H₂ TREATMENT, 410-I (MELT 52)

410-I (M 52)	°C	Time (hr)	°C	Time (hr)	Gas Cooled	Wt Loss (mg)	Au/Elec R (M Ω)
-A	460	6 $\frac{1}{2}$			A	0.9	5.5
-B	460	7			A	1.4	5.6
-C	560	2			A	73.4	0.016
-D	480	7			A	7.0	0.5
-E	500	2			A	0.8	1.24
-F	430	7			A	1.2	7.3
-G	500	2			H ₂	24.0	1.6
-H	480	4			H ₂	2.3	21.0
-I	480	6			H ₂	3.6	12.5
-J	500	1			H ₂	2.0	24.0
-K	430	6 $\frac{1}{4}$			H ₂	0.7	105
-L	450	6			H ₂	0.9	16.0
-M	505	1	460	4	H ₂	0.7	38.0
-N	500	1	480	4	H ₂	0.7	28.0
-O	550	1	460	4	H ₂	16.6	2.0
-P	450	6			A	0.9	16.0
-Q	460	4	500	1	H ₂	2.2	16.0
-R	430	4	500	1	H ₂	0.6	14.5
-S	400	4	500	1	H ₂	0.7	500
-T	430	4	520	1	H ₂	1.4	7.5
-U	460	4	520	1	H ₂	1.3	9.5

TABLE 3 H₂ TREATMENT, 410-DJ

410-DJ (M 4)	°C	Time (hr)	Cooling Gas	Wt Loss (mg)	Au/Elec R(M Ω)
-2	400	3	A}	0.5	
	405	7	A}		
-3	600	3 $\frac{1}{2}$	A	226.4	3.3 x 10 ⁻⁴
-4	420	7	A	1.3	
-5	440	7	A	0.4	82
-6	460	7	A	1.3	450
-7	500	7	A	0.1	3.9
-8	480	7	A	0.2	10
-9	600	$\frac{1}{2}$	A	79.8	0.019
-10	600	1 $\frac{1}{3}$	A	149.9	1.3 x 10 ⁻³
-11	520	7	A	0.7	0.8
-12	600	$\frac{1}{2}$	A	20.3	0.023
-14	540	7	A	23.8	0.2
-15	420	7	A	1.7	330
-16	420	7	A	2.0	200
-2 (Second Treat- ment)	600	1/12	A	0.5	2.5
410-DJ (M2-1)	450	7	A	0.6	8.0
-DJ (M2-2)	480	5	A	0.3	0.9
-DJ (M2-3)	500	7	A	1.2	0.4
-DJ (M2-4)	520	7	A	20.5	

TABLE 4 H₂ TREATMENT, 410-DJ (MELT 6)

410-DJ(M6-1)	°C	Time (hr)	°C	Time (hr)	Cooling Gas	Wt Loss (mg)	Au/Elec R(M Ω)
-A	450	7			A	1.0	430
-B	480	7			A	-	2.6
-C	520	7			A	0.6	1.5
-D	460	4	520	2	A	0.3	17
-E	480	4	520	1	N ₂	0.4	82
-F	480	4	520	2	A/N ₂	0.7	2.6
-G	500	7			A	1.0	460
-H	540	4			A	1.3	1.2
-I	540	7			A	4.3	0.7
-J	500	7			A	2.0	0.3
-K	600	$\frac{1}{2}$			A	1.1	0.9
-L	600	10 min			A	1.3	1.2
-N	RT → 500°C/A; 500-600/H ₂ (OFF) HELD AT 547°C 2 $\frac{1}{4}$ hr/A					2.5	220
-O	UNTREATED						17,000
-P	600	$\frac{1}{2}$			A	7.4	--
410-DJ							
(M6-II-A)	560	4			A	4.5	0.2
(M6-II-C)	580	4			A	89.6	0.0007
(M6-II-D)	580	6			A	265.9	0.0004

TABLE 5 H₂ TREATMENT, 410-EA (MELT 2) AND 410-EC (MELT 2)

410-EA(M 2)	°C	Time (hr)	Cooling Gas	Wt Loss (mg)	Au/Elec R (M Ω)
-A	440	6	A	3.3	--
-B	460	6	A	3.5	--
-C	480	6	A	3.3	--
-D	500	6	A	2.7	--
-E	520	6	A	7.0	--
-F	540	6	A	11.3	--
410-EC(M 2)					
-A	480	6	A	4.0	6.6
-B	500	6	A	1.1	31.0
-C	520	6	A	1.2	6.0
-D	560	6	A	0.7	9.4
-E	580	6	A	1.8	0.4
-F	460	6	A	1.5	52.0

TABLE 6 H₂ TREATMENT, 410-EE (MELT 1) AND 410-EF (MELT 1)

410-EE (M 1)	°C	Time (hr)	Cooling Gas	Wt Loss (mg)	Au/Elec R (M Ω)
-A	450	6	A	1.0	160
-B	480	6	A	1.5	9.0
-C	520	4	A	1.9	3.5
-D	443	7	A	1.2	35
-E	440	3	A	0.2	750
-F	440	1	A	0.2	10,300
-G	550	1	A	0.4	77
-H	600	1	A	2.3	0.08
410-EF (M 1)					
-A	480	2	A	5.1	21,000
-B	460	2	A	1.5	200
-C	480	6	A	1.4	17
-D	500	6	A	1.8	27
-E	520	6	A	3.2	9.4
-F	540	6	A	3.3	3.0
-G	560	6	A	1.9	5.4
-H	580	6	A	6.3	1.2

ELECTRICAL CHARACTERIZATION

After the elemental germanium film had been precipitated in the surface of its respective glass, gold electrodes were vapor deposited through a mask so there was one cm between them. The electrodes were one cm long, therefore the surface area between the electrodes was one cm². Electrical leads were soldered to the gold electrodes by means of a silver epoxy. Resistance measurements were made using a Keithley Model 610C electrometer. One Hall measurement was made at the New York Institute of Technology by Prof. I. Cadoff.

X-RAY DIFFRACTION

X-ray diffraction characterization was made with a Picker Model 3488K unit.

PHOTOEXCITATION EXPERIMENTS

The photoexcitation experiments were carried out by utilizing the following light sources: a 250 watt infrared bulb, a 300 watt incandescent bulb, and a 500 watt incandescent bulb. The photo-voltage responses were recorded with the Model 610C Keithley electrometer. The lamp source was placed 15 cm above each of the electroded germanium film samples. The results were obtained for room temperature conditions, under a 15 second exposure limitation.

RESULTS

GLASS PREPARATION

All of the glasses listed in Table 1 melted to relatively good quality products. The annealed glasses from compositions 410-I, 410-DJ, 410-EA, 410-EB, 410-EC, and 410-ED were transparent to visible light; however, glasses 410-EE and 410-EF yielded dense black opals. The glasses formed the opals as they cooled to the annealing temperature and did not opalize in the annealer. Polarimetric observation of the transparent samples indicated that they were stress free, however birefringence did appear in all of the samples and it was associated with glass inhomogeneity due to the lack of stirring in the molten state.

FILM PREPARATION

All of the samples that developed good quality germanium films lost weight; reference to Tables 2-6 reflect this observation. Most of the films had a mirror finish; however, any inhomogeneity in parent glass showed up as a chordy area in the film.

FILM OPTICAL CHARACTERIZATION

All of the films listed in Tables 2-6 were subjected to microscopic examination on the Reichert reflection microscope. Figures 1 through 6 represent germanium film formations which will be discussed in more detail in the following section. Figures 1 through 3 represent films that were precipitated in the surface of glass 410-I. Figures 4 through 6 depict representative film types precipitated in the surface of glass 410-DJ.

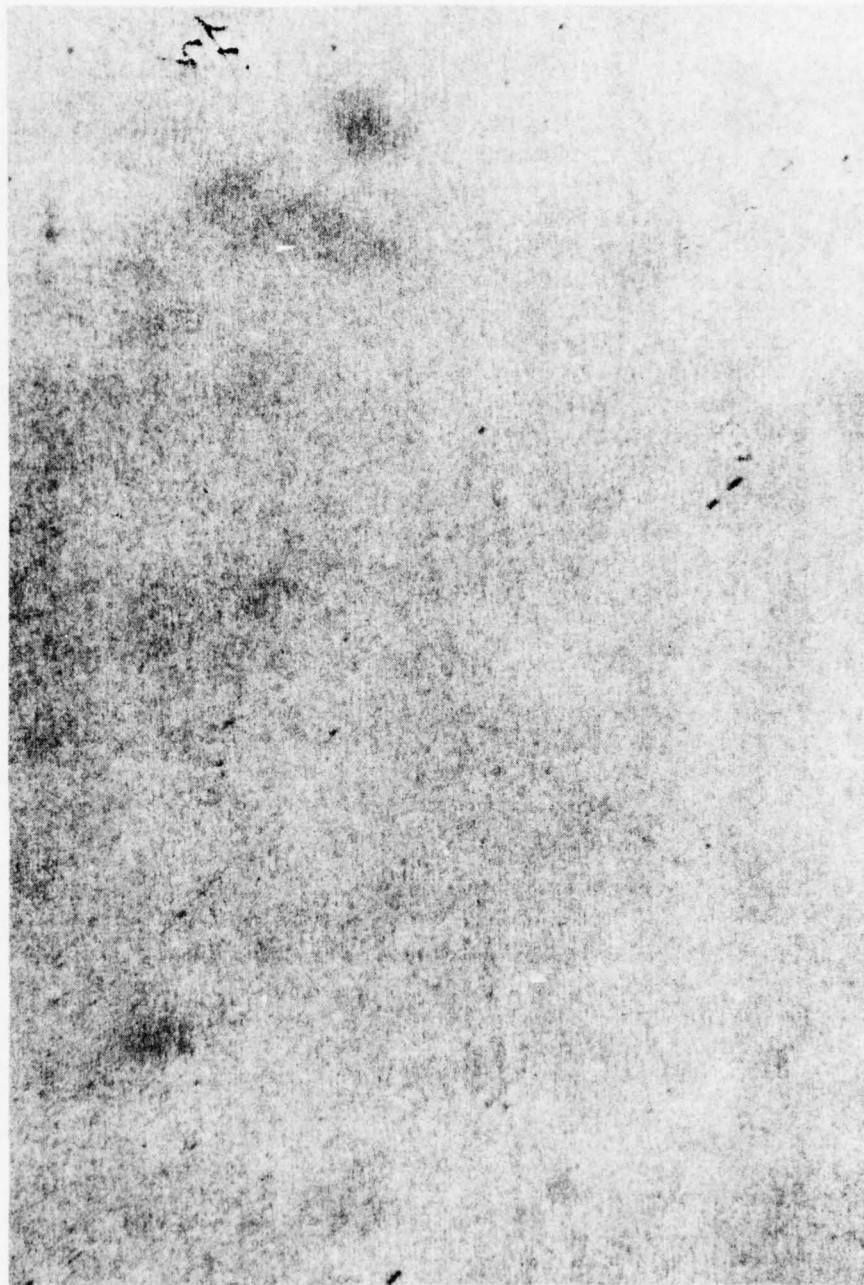


Fig. 1 Photomicrograph of Germanium Film Formed on Glass
410-I (Melt 52-K), 430°C - 6 hr 15 min/H₂,
1 cm = 33 μ m

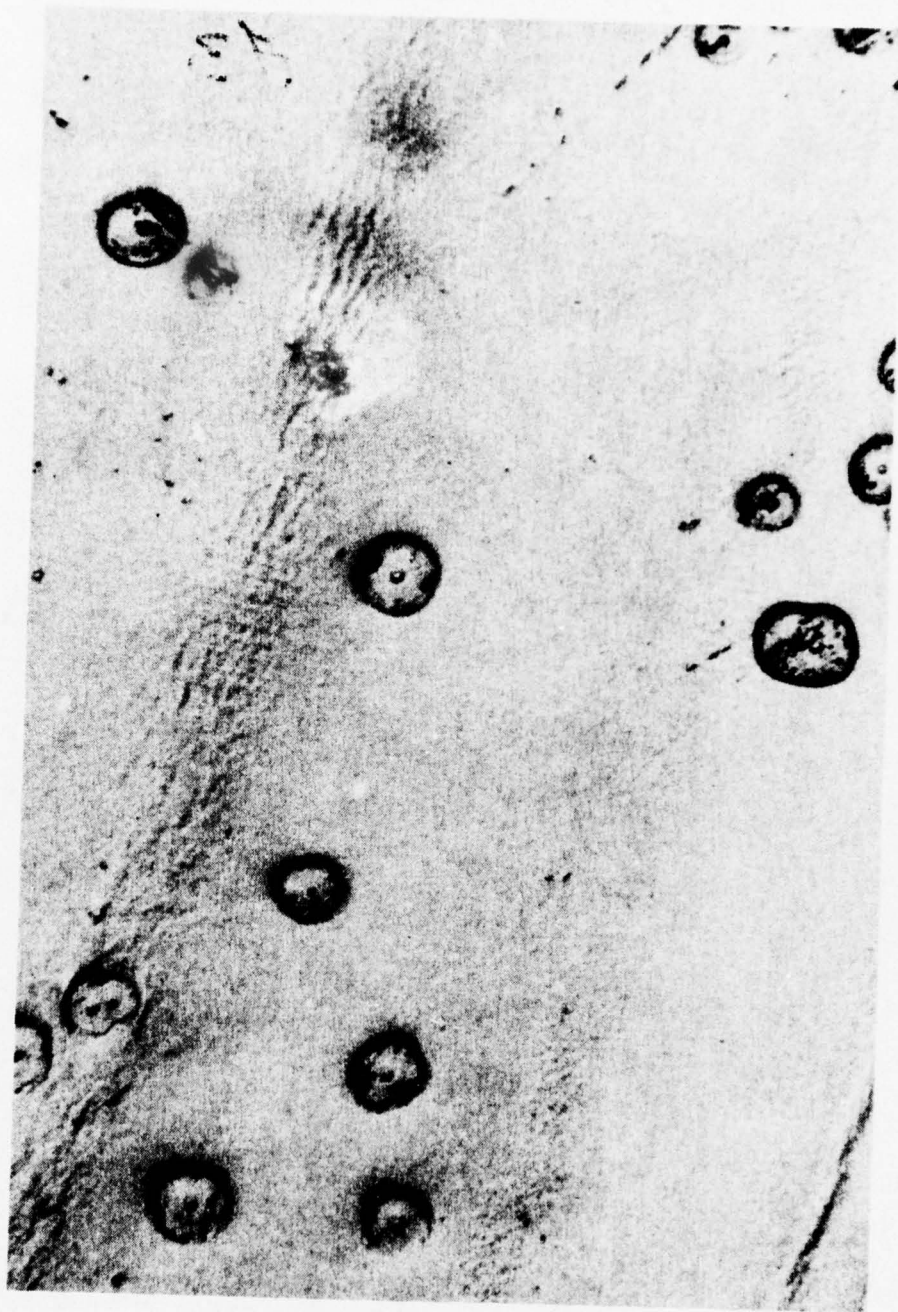


Fig. 2 Photomicrograph of Germanium Film Formed on Glass 410-I (Melt 52-L), 450°C - 6 hr/H₂, 1 cm = 33 μm



Fig. 3 Photomicrograph of Germanium Film Formed on Glass 410-DJ (Melt 52-I), 480°C - 6 hr/H₂, 1 cm = 33 μm

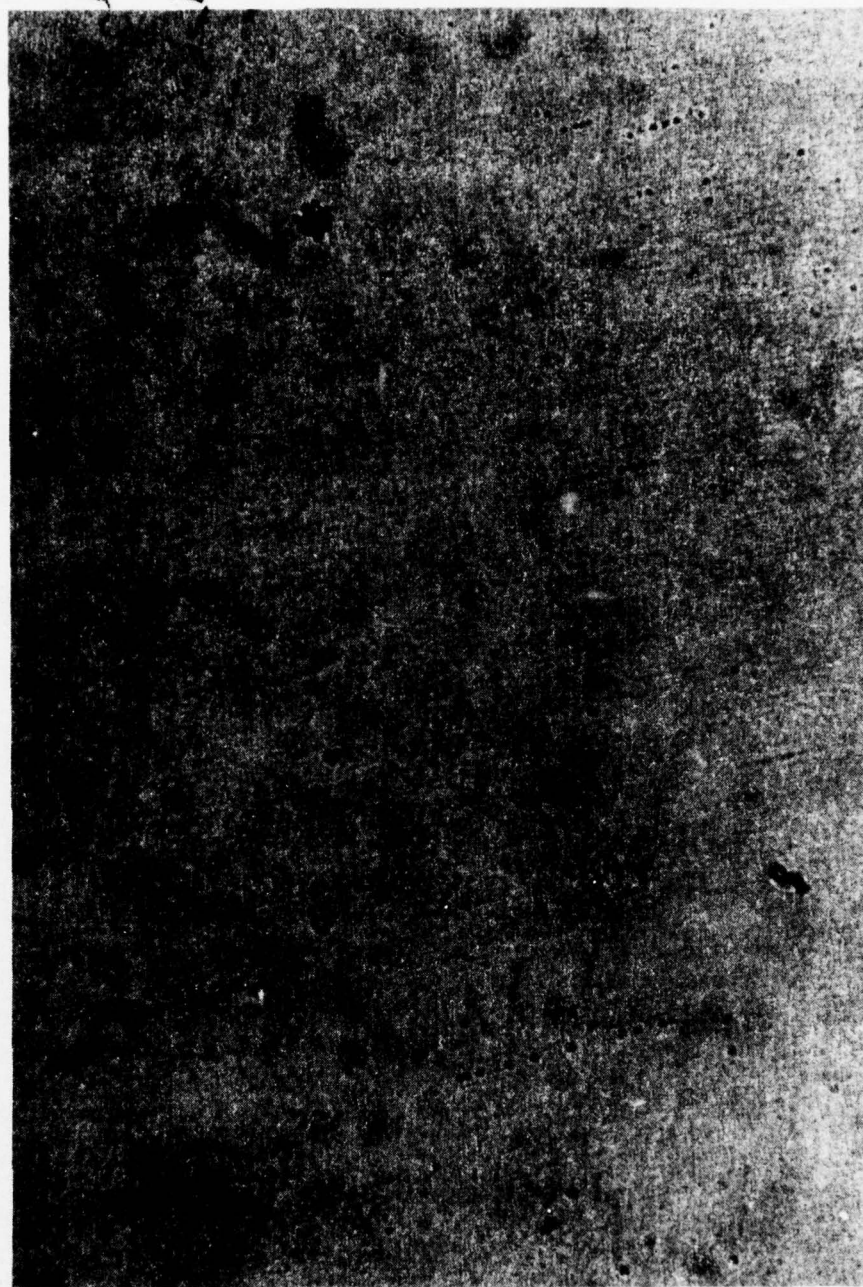


Fig. 4 Photomicrograph of Germanium Film Formed on Glass 410-DJ (Melt 4-15), 420°C - 7 hr/ H_2 , 1 cm = $33\text{ }\mu\text{m}$



Fig. 5 Photomicrograph of Germanium Film Formed on Glass 410-DJ (Melt 2-3), 500°C - 7 hr/H₂, 1 cm = 33 μ m



Fig. 6 Photomicrograph of Germanium Film Formed on Glass 410-DJ (Melt 4-3), $600^{\circ}\text{C} - 3\frac{1}{2} \text{ hr}/\text{H}_2$, $1 \text{ cm} = 33 \mu\text{m}$

ELECTRICAL CHARACTERIZATION

Gold electrodes were vapor deposited on the germanium films as described in the experimental section. Surface resistance measurements were completed utilizing the Keithley Model 610-C electrometer. The results are recorded in Tables 2-6. Gold electrodes were employed because they have been reported to give ohmic contacts with germanium (Ref. 6). The resistance measurements were observed to be stable for each of the respective samples. A Hall effect measurement was performed on one film sample, namely that prepared from glass 410-DJ (M4-4). X-ray diffraction and optical examination indicated that the film was amorphous germanium and reported to be p-type.

X-RAY DIFFRACTION

Three X-ray diffraction traces (Figs. 7, 8, and 9) exhibit the results for the amorphous and crystalline state of films developed on glass 410-I. The X-ray diffraction pattern for the base glass of 410-I is shown in Fig. 10.

PHOTOEXCITATION EXPERIMENTS

In order to cull the information available and present it in a coherent form, the nonresponding samples have been eliminated. Tables 7 and 8 exhibit a comparison of the photovoltage activity as found for an exposure of 15 seconds to the respective illumination.

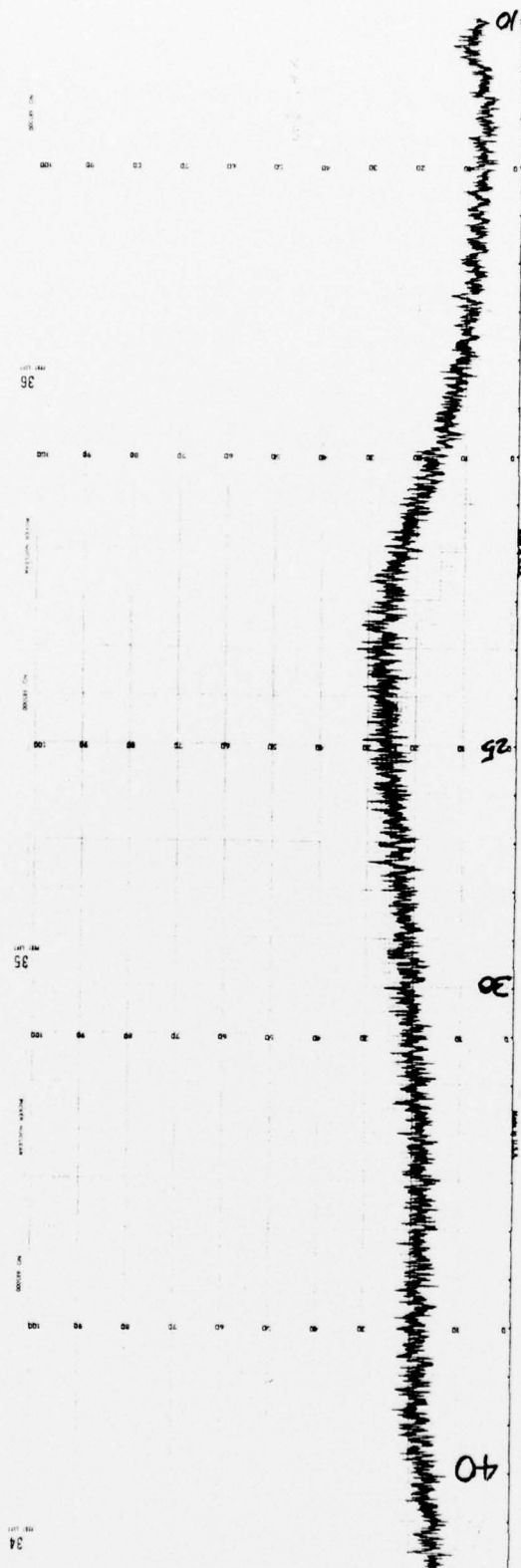
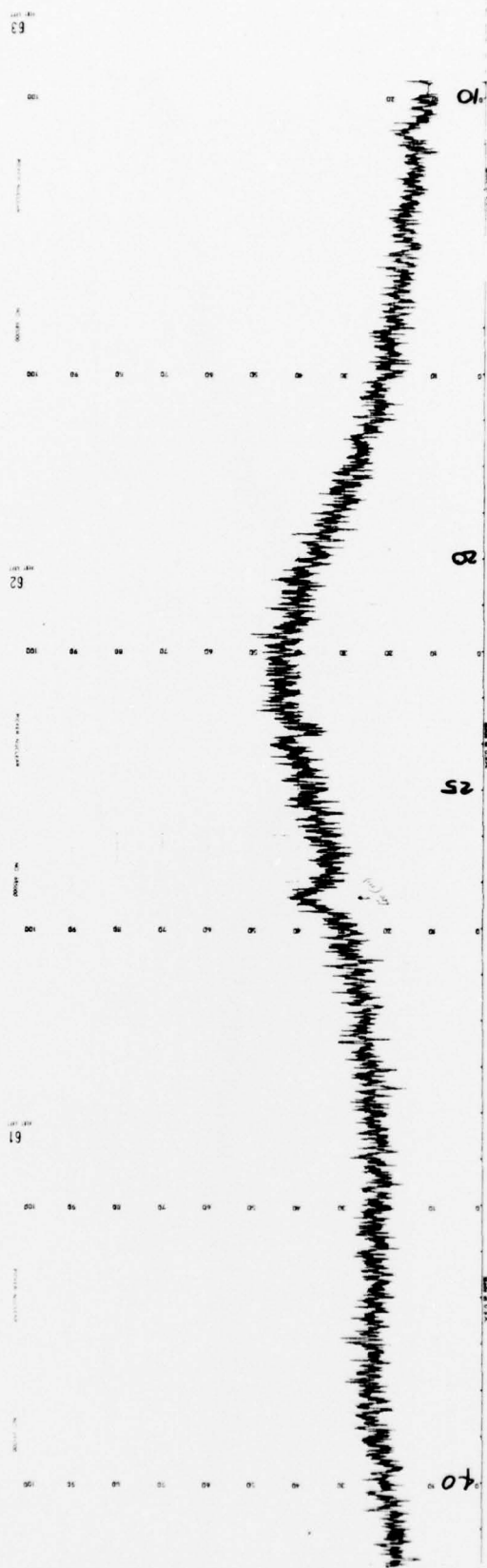


Fig. 7 X-Ray Diffraction Pattern for Germanium Film
Formed on Glass 410-I, 400°C - 24 hr/H₂



2 θ Values

Fig. 8 X-Ray Diffraction Pattern for Germanium Film
Formed on Glass 410-I, 500°C - 2 hr/H₂

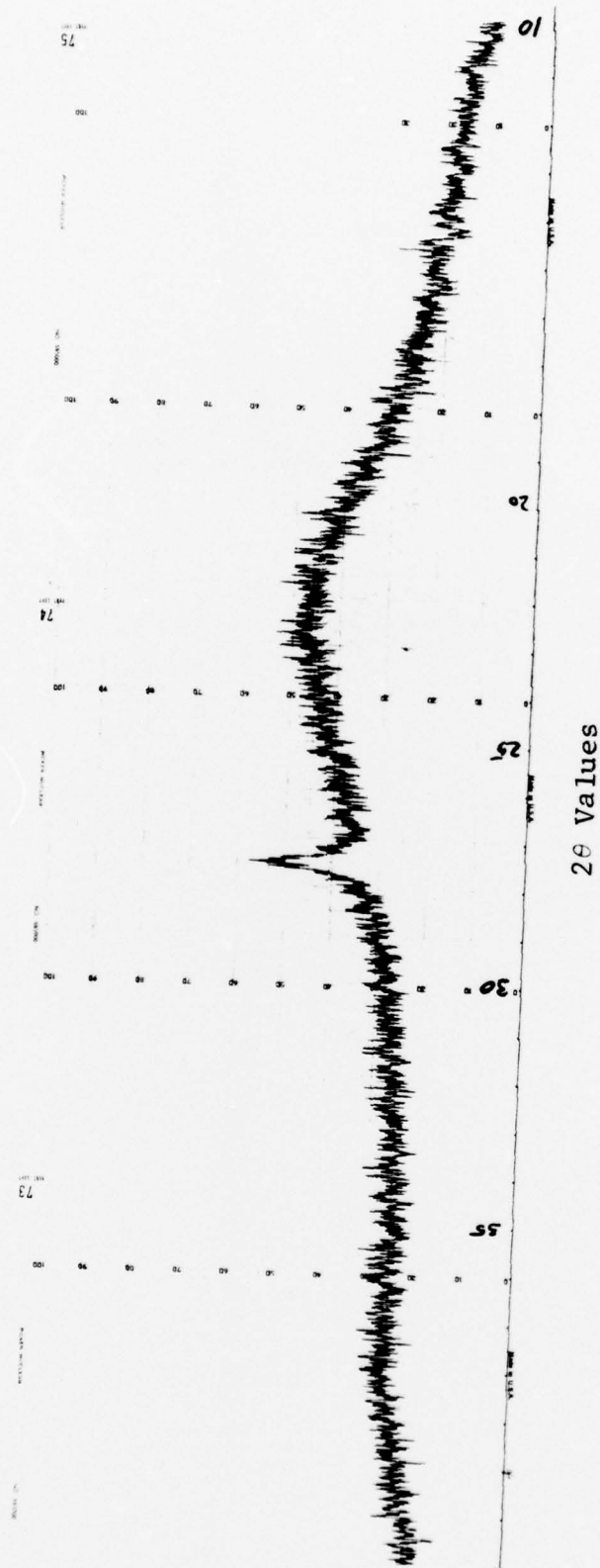
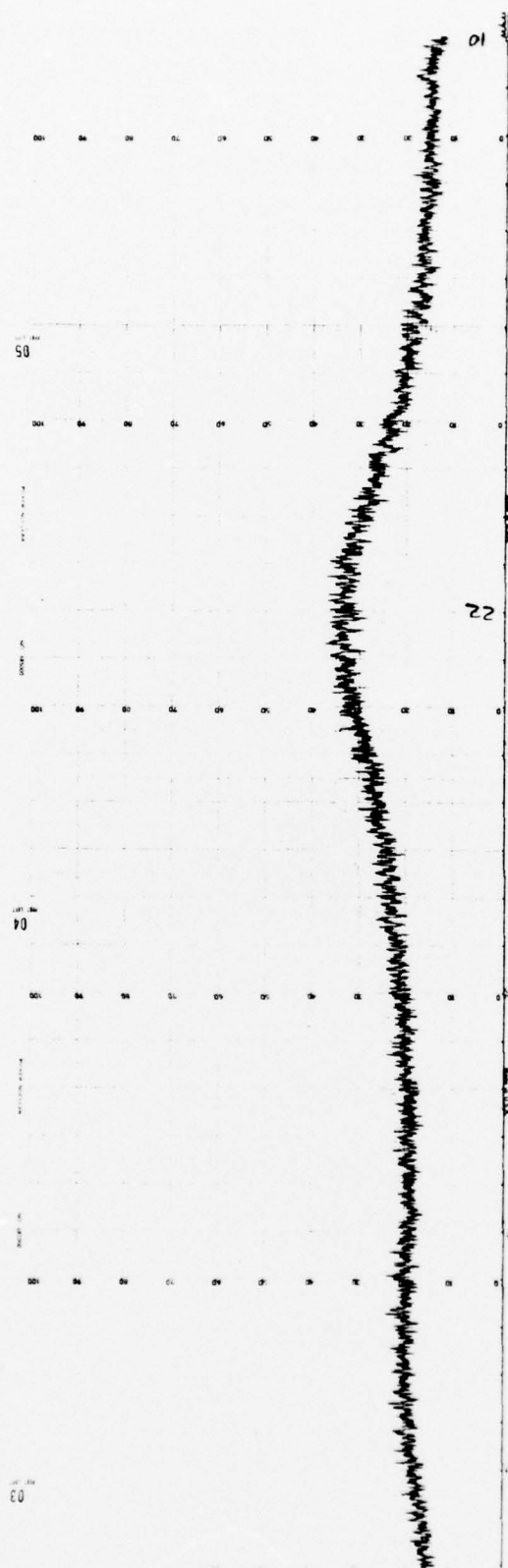


Fig. 9 X-Ray Diffraction Pattern for Germanium Film
Formed on Glass 410-I, 500°C - 7 hr/H₂



2θ Values

Fig. 10 X-Ray Diffraction Pattern for Glass 410-I,
Untreated

TABLE 7 COMPARISON OF 15 SECOND EXPOSURE Δ EMF GE FILM
RESPONSES (mv), GLASSES 410-I, -DJ

Sample	250 Watt Infrared	300 Watt Incandescent	500 Watt Incandescent	Dark R (ohms)
410-I (M52-B)	0.3			5.6×10^6
-I (M52-C)	0.1	0.05		0.016×10^6
-I (M52-D)	0.1	0.1		0.5×10^6
-I (M52-E)	0.3	0.1	0.4	1.3×10^6
-I (M52-G)			0.3	1.7×10^6
-I (M52-I)	1.5			17×10^6
-I (M52-O)	0.1			3×10^6
-I (M52-T)		0.3		7.5×10^6
410-DJ (M2-1)			0.2	1.1×10^6
-DJ (M2-2)	0.55	0.1	0.5	10.3×10^6
-DJ (M2-3)	0.2	0.5	0.6	0.4×10^6
-DJ (M2-2)	0.3	0.2	0.5	2.5×10^6
-DJ (M4-3)	0.4		0.1	500
-DJ (M4-5)	0.3			91×10^6
-DJ (M4-9)	0.2		0.1	0.029×10^6
-DJ (M4-10)	0.2	0.1		0.01×10^5
-DJ (M4-11)	0.15		0.1	0.88×10^6
-DJ (M4-12)	0.7	0.1	0.2	0.3×10^5
-DJ (M4-14)	0.4	0.2	0.4	0.28×10^6
-DJ (M6-1-B)			0.3	2.2×10^6
-DJ (M6-1-F)		0.1		2.6×10^6

TABLE 8 COMPARISON OF 15 SECOND EXPOSURE Δ EMF GE FILM
RESPONSES (mv), GLASSES 410-DJ, -EE, -EC, -EF

Sample	250 Watt Infrared	300 Watt Incandescent	500 Watt Incandescent	Dark R (ohms)
410-DJ (M6-1-H)	0.1		0.1	1.2×10^6
-DJ (M6-1-I)	0.5	0.1	0.3	0.71×10^6
-DJ (M6-1-J)	0.5	0.1	0.2	0.21×10^6
-DJ (M6-1-K)	1.0	0.3	0.7	0.9×10^6
-DJ (M6-1-L)	0.4	0.1	0.3	1.2×10^6
-DJ (M6-1-N)			15.0	150×10^6
-DJ (M6-II-A)	0.6	0.1	0.2	0.2×10^6
-DJ (M6-II-C)	0.7	0.5	0.6	0.007×10^5
-DJ (M6-II-D)	0.4		0.1	0.004×10^5
410-EE (M1-H)	0.15		0.1	0.08×10^6
410-EC (M2-B)		1.2	7.0	29×10^6
-EC (M2-D)			1.0	7.5×10^6
-EC (M2-E)		0.1	0.6	0.38×10^6
-EC (M2-C)		0.2		6×10^6
410-EF (M1-D)	1.0		0.5	27×10^6
-EF (M1-C)	0.7			21×10^6
-EF (M1-F)	0.1	0.1	0.6	2.9×10^6
-EF (M1-H)			0.5	1.2×10^6

DISCUSSION

A discussion of film formation based upon vapor deposition is considered an unnecessary action. Therefore, this section will be devoted to the precipitated film formation of germanium. It appears that the surface of a typical oxygen deficient germanate glass composition reacts with hydrogen and releases water as a by-product. This is substantiated by the fact that each sample that formed a good film lost weight. M. Kastner and H. Fritsche (Ref. 15) have found that water can be transmitted through an amorphous film of germanium much more readily than a polycrystalline film. Since the micrographs from Figs. 2, 3, and 5 illustrate that some films developed in the present experiments were hybrids (namely amorphous and partially crystalline) a deduction can be made. A water by-product formed at the reaction interface and was expelled by different mechanisms through the amorphous and crystalline zones. For example, when the amorphous film started to crystallize at its softening point, a portion of the water exited through the more densified crystalline areas. This is readily apparent in Fig. 5, where an analogy to volcanic activity can be seen. These zones are known as "hillocks." However, in the amorphous films of Figs. 1 and 4, no "hillock" formation is observed, therefore the reaction byproduct, water, left the system unhindered. This observation relates to Kastner and Fritsches's results (Ref. 15) on water diffusion through amorphous germanium films. The micrograph from Fig. 6 illustrates a film that has effectively become completely polycrystalline.

Figure 7 represents a typical X-ray trace for an amorphous germanium film prepared from glass 410-I. This glass had been held at 400°C - 24 hours in hydrogen. No crystalline peaks were observed. Its photomicrograph was similar to the one shown in Fig. 1,

namely, no hillock formation was observed. Figures 8 and 9 show the X-ray diffraction traces for two samples of glass 410-I that had been heat treated in hydrogen at 500°C (Fig. 8 for 2 hours and Fig. 9 for 7 hours). The germanium (111) peak is readily apparent in each. Qualitatively, Fig. 9 can be considered to exhibit more crystallinity. The photomicrographs associated with the 410-I films from Figs. 8 and 9 showed hillock formation. For comparison purposes, Fig. 10 represents an X-ray diffraction trace of an nonhydrogen treated surface of glass 410-I.

A brief discussion of the surface resistance measurements reported for the samples shown in Tables 2-6 is in order. As noted in the previous sections, gold electrodes (one cm apart) were vapor deposited on each of the germanium film samples in order to create a means of comparing the resistance values. It was not possible to obtain the film thickness without destroying the sample, therefore the surface resistance over a constant area (1 cm^2) was used for a general comparison. All of the resistance measurements taken with the Keithley Model 610C electrometer exhibited constant readings under room temperature conditions. However, reference to Tables 2-6 shows a large range in these values. Based on many photomicrographic observations and paralleling the discussions of the preceding paragraphs, it is believed that the higher resistance values ($> 100 \times 10^6 \Omega$) represent films in the amorphous state, while those lower values ($< 100 \times 10^6 \Omega$) represent films with varying amounts of crystallinity. The extremely low resistance values (100-1000 Ω) are identified with the most crystalline of the germanium films.

Finally, the photoexcitation results shown in Tables 7 and 8 have been limited to those films which exhibited reproducible, nonerratic responses during the 15 second exposure sequence. It can be seen that photovoltages were obtained for both high and low

resistance films. The highest photovoltage was found for a sample film (410-DJ-M6) with the highest dark resistance. The balance of the film samples that were formed and noted in Tables 2-6 were eliminated because stable photovoltage responses could not be obtained.

Since the germanium film program has been placed in abeyance for the moment, there was not time to develop a more basic understanding of the physical-chemical-electronic reasons for the photo-responses of some of the prepared germanium films. However, in the future, this would be a good place to continue. For this reason, the original film sample designations have not been changed.

SUMMARY

Reasonably homogeneous oxygen deficient germanate base glasses have been prepared and finished into samples which were subjected to a series of hydrogen treatments within and above the transformation ranges of the respective glasses. Amorphous, partially crystalline, and highly crystalline germanium films have been optically characterized and subjected to comparative surface resistance measurements. Photoexcitation experiments have been employed to cull out the more responsive photovoltage producing films. Any future effort in this area would require a more basic study of the physical-chemical-electronic characteristics of these films, in order to pursue the best avenues of application.

REFERENCES

1. Kivlighn, H. Jr., "Novel Glasses and Processes for the Preparation Thereof," U.S. Patent No. 3,824,123, July 16, 1974.
2. Kivlighn, H. Jr., The Insitu Formation of Germanium Thin Films, Grumman Research Department Memorandum RM-526, December 1971.
3. Pócza, J. F., Barna, Á., Barna, P. B., Pozsgai, I., and Radnóczy, G., "Insitu Electron Microscopy of Thin Film Growth," Proc. 6th International Vacuum Congr., Japan, 1974; also J. Appl. Phys. Suppl. 2, Part 1, p. 525, 1974.
4. Barna, Á., Barna, P. B., and Pócza, J. F., "Crystallization Processes in a-Ge Thin Films," J. of Non-Cryst. Solids, Vol. 8-10, p. 36, 1972.
5. Barna, Á., Barna, P. B., Bodó, Z., Pócza, J. F., Pozsgai, I., and Radnóczy, G., "Simultaneous Investigation of the Crystal Structure and Electrical Properties of Crystallized Germanium Films by UHV Insitu Electron Microscopy," Thin Solid Films, Vol. 23, p. 49, 1974.
6. Johannessen, J. S., "The Amorphous-Crystalline Transition in Germanium Films," Phys. Stat. Sol. (A), Vol. 26, p. 571, 1974.
7. Barna, Á., Barna, P. B., Bodó, Z., Pócza, J. F., Pozsgai, I., and Radnóczy, G., "Structure, Ordering, and Electrical Conduction of High Purity Amorphous Ge Films," Proc. 5th International Conference on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen, p. 109, September 1973.
8. Barna, Á., Barna, P. B., Pócza, J. F., Pozsgai, I., and Dévényi, A., "Thick Self-Supporting Amorphous Germanium Films," Nuclear Instruments and Methods, Vol. 102, p. 549, 1972.

9. Johannessen, J. S., "Thickness Dependence of σ of Thin Germanium Films," Phys. Stat. Sol. (A), Vol. 26, p. K53, 1974.
10. Fischer, J. E., "Photoelectric Properties of Amorphous Silicon and Germanium Films," Thin Solid Films, Vol. 17, p. 223, 1973.
11. Valkiainen, M., Tiainen, O. J. A., Suntola, T., and Naakka, H., "A Study of Dielectric Properties of Untreated, Heat-Treated, and Irradiated Amorphous Germanium," Phys. Stat. Sol. (A), Vol. 23, p. K63, 1973.
12. Hirose, M., Suzuki, T., Yoshifuji, S., and Osaka, Y., "Electrical and Optical Properties of Amorphous Germanium," Japan. J. of Appl. Phys., Vol. 13, No. 1, p. 40, 1974.
13. Kallmann, H., Spruch, G. M., and Trester, S., "Photovoltages Larger than the Band Gap in Thin Films of Germanium," J. Appl. Phys., Vol. 43, No. 2, p. 469, 1972.
14. Ma, W., Anderson, R. M., and Hruska, S. J., "Study of the Anomalous High Photovoltaic Effect in Germanium Thin Films," J. Appl. Phys., Vol. 46, No. 6, p. 2650, 1975.
15. Kastner, M. and Fritsche, H., "Ambient Induced Changes of the Conductance of Amorphous Germanium," Mater. Res. Bull., Vol. 5, p. 631, 1970.